Glancing Angle Deposited Platinum Nanorod Arrays for Oxygen Reduction Reaction

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ABSTRACT

In this work, we investigated the electrocatalytic oxygen reduction reaction (ORR) activity of vertically aligned, single-layer, carbon-free, and single crystal Pt nanorod arrays utilizing cyclic voltammetry (CV) and rotating-disk electrode (RDE) techniques. A glancing angle deposition (GLAD) technique was used to fabricate 200 nm long Pt nanorods, which corresponds to Pt loading of 0.16 mg/cm\textsuperscript{2}, on glassy carbon (GC) electrode at a glancing angle of 85\textdegree; as measured from the substrate normal. An electrode comprised of conventional carbon-supported Pt nanoparticles (Pt/C) was also prepared for comparison with the electrocatalytic ORR activity and stability of Pt nanorods. CV results showed that the Pt nanorod electrocatalyst exhibits a more positive oxide reduction peak potential compared to Pt/C, indicating that GLAD Pt nanorods are less oxophilic. In addition, a series of CV cycles in acidic electrolyte revealed that Pt nanorods are significantly more stable against electrochemically-active surface area loss than Pt/C. Moreover, room temperature RDE results demonstrated that GLAD Pt nanorods exhibit higher area-specific ORR activity than Pt/C. The enhanced electrocatalytic ORR activity of Pt nanorods is attributed to their larger crystallite size, single-crystal property, and the dominance of (110) crystal planes on the large surface area nanorods sidewalls, which has been found to be the most active plane for ORR. However, the Pt nanorods showed lower mass specific activity than the Pt/C electrocatalyst due to the large diameter of the Pt nanorods.

INTRODUCTION

Polymer electrolyte membrane (PEM) fuel cells are electrochemical energy conversion devices that have attracted great interest as a primary power source for electric vehicles due to their relatively low operating temperature, high efficiency, and low emissions [1-3]. However, the high cost of the noble metal (e.g., Pt) electrocatalysts used in PEM fuel cells is one of the major barriers to their commercial viability. Compared to anodic hydrogen oxidation reaction (HOR), the oxygen reduction reaction (ORR) at the cathode is a sluggish reaction and typically the major contributor to the efficiency loss in an operating PEM fuel cell [1-4]. Typical cathode and anode electrocatalysts are comprised of layers of platinum catalyst nanoparticles (3-5 nm in
size) supported on carbon black [3]. In addition to the cost issue, this type of electrocatalyst faces other challenges related to the carbon support, summarized as follows: Oxidation of the carbon support causes catalyst loss [5], the carbon support facilitates the formation of peroxide species that lead to degradation of the membrane polymer [6], and carbon separates from the ionomer over time, leading to loss of effectiveness [5]. Therefore, extensive effort is currently underway to develop high-performance, durable, carbon-free, and low cost (low Pt loading) electrocatalyst materials [7]. For example, 3M has demonstrated improved durability and area-specific activity of nano-structured thin film (NSTF Pt) electrocatalyst layers consisting of large-grained polycrystalline Pt thin films deposited on and encapsulating oriented crystalline whiskers of an organic pigment material [8]. However, the polycrystalline nature of Pt thin films has the disadvantages of being prone to oxidation at the grain boundaries [9] and of being comprised of a mixture of low index planes with varying ORR activities. The (111) plane is the energetically-favorable growth plane of Pt films. Single-crystal data of Markovic et al. [10] showed that the ORR activity of different crystal planes of platinum in perchloric acid electrolyte follows the trend Pt(110)>Pt(111)>Pt(100), with relative ORR activities of approximately 1.5, 1.2, and 0.6 as compared to polycrystalline Pt [11]. In sulfuric acid electrolyte the activity trend was found to be Pt(110)>Pt(100)>>Pt(111) [10]. In another study, Chen et al. [12] reported that enhanced ORR electrocatalytic activity of Pt nanotubes in 0.5 M H2SO4 might be attributed to preferential exposure of certain crystal facets of nanotubes. Therefore, controlling the electrode porosity, having a single-crystal property, and controlling the crystal orientation by promoting the Pt[110] orientation over the Pt[111] orientation may further enhance the electrochemical activity of PEM fuel cell cathodes.

In this paper, we employed detailed CV and RDE measurements for investigating the electrocatalytic ORR activity of carbon-free, single layer, and single-crystal Pt nanorod arrays produced by the glancing angle deposition (GLAD) technique. The GLAD technique provides a novel capability for growing 3D nanostructure arrays with interesting material properties [13-16]. It offers a simple, single-step, cost and time efficient method to fabricate nanostructured arrays of various elemental materials as well as alloys and oxides. The GLAD technique uses the “shadowing effect,” which is a “physical self-assembly” process through which obliquely incident atoms/molecules preferentially deposit on the tops of higher surface points, such as on the tips of a nanostructured array or on the hill-tops of a rough or patterned substrate.

EXPERIMENTAL WORK

We employed a DC magnetron sputtering system (Excel instruments, India) for the fabrication of Pt nanorod arrays for a growth time of 30 minutes, which resulted in 200 nm long Pt nanorods. The depositions were performed on glassy carbon substrate using a 99.99 % pure Pt cathode (diameter ~ 2.54 cm). The substrates were mounted on the sample holder located at a distance of about 12 cm from the cathode. The base pressure of about 2.4 × 10⁻⁶ Torr was achieved using a turbo-molecular pump backed by a mechanical pump. In all deposition experiments, the power was 150 Watts with an ultra pure Ar working gas pressure of 2.4 × 10⁻³ Torr. The substrates were tilted so that the angle between the surface normal of the target and the surface normal of the substrate was 85°. During GLAD, the substrates were also rotated around their surface normal with a speed of 2 rpm. The deposition rate of GLAD Pt nanorods (i.e. length
per deposition time) was about 7.5 nm/min as measured by the analysis of cross-sectional scanning electron microscopy (SEM) images.

The weight loadings of Pt nanorods were measured utilizing a quartz crystal microbalance (QCM, Inficon-Q-pod QCM monitor, crystal: 6 MHz gold coated standard quartz) set-up [17]. For this purpose, we deposited GLAD Pt nanorods directly on QCM crystals and measured the loading values by comparing the oscillation frequencies of the blank and coated crystal. The surface morphology and crystallographic structure of Pt nanorods have been studied using SEM (FESEM-6330F, JEOL Ltd, Tokyo, Japan) and X-ray diffraction (XRD) system (Bruker D8 discover), respectively.

The electrochemical tests (CV and RDE) were performed in deaerated and oxygen-saturated 0.1 M HClO₄ at room temperature for characterizing the catalyst ORR activity of the Pt nanorods and Pt/C electrocatalysts. The test setup was a typical three-electrode system (Pine Instrument bipotentiostat, North Carolina, USA), consisting of a working electrode (Pt nanorods or Pt/C on glassy carbon), a Pt wire counter electrode, and a Ag/AgCl reference electrode. All the potentials in the remainder of the paper are reported with respect to reversible hydrogen electrode potential (RHE). The area of the working electrode samples was 0.196 cm², while the area of the counter electrode was higher to allow for a more uniform current density distribution through the working electrode. The working electrodes were scanned from 0 to +1.15 V in O₂-free 0.1 M HClO₄ at a scan rate 50 mV/s. For chemical stability in the acidic environment, the electrodes were also scanned multiple times in the 0.6 to 1.0 V range at 50 mV/s. RDE measurements were performed at room temperature in oxygen-saturated 0.1 M HClO₄ electrolyte at a scan rate 20 mV/s and a rotation speed of 1600 rpm.

For comparison, the conventional carbon-supported Pt nanoparticle electrode (Pt/C 20% wt Pt on carbon-black, Clean Fuel Cell Energy, LLC) was prepared as described by Schmidt et al. [18]. In short, 20 μl of aqueous suspension of 1 mg catalyst/ml, which was obtained by ultrasonic mixing for approximately 20 minutes, was pipetted onto a clean glassy carbon disk electrode (5 mm diameter, Pine Instrument Inc.), leading to Pt loading of ~20 μg/cm². After evaporation of the water at room temperature, 20 μl of a diluted Nafion™ solution (5% wt, Clean Fuel Cell Energy, LLC) was pipetted on the electrode surface in order to attach the catalyst particles onto the glassy carbon substrate. The Nafion loading was about 0.1 μm which was in the range where diffusion limitations of Nafion was considered negligible [19]. After preparation, the electrodes were immersed in deaerated (Argon, Airgas) 0.1 M HClO₄ under potential control of 0.5 V. The potential was then cycled between 0 to 1.15 V at a scan rate 50 mV/s in order to produce an electrochemically-clean electrode surface.

RESULTS AND DISCUSSION

Figure 1 shows the top view and side view SEM images of 200 nm long Pt nanorods. In these images, an isolated columnar morphology of Pt nanorods can be clearly seen. The isolated nature of the rods in lateral directions leads to a channeled porosity aligned in the vertical direction to the substrate surface. This novel geometry can greatly help effective transportation of the hydrogen molecules to the catalyst sites in the anode and, more importantly, with proton and oxygen transport in the cathode layer. Moreover, high resolution top view SEM analysis of Pt nanorods shown in Fig. 1 reveals that some of the rods in fact have 6-fold symmetric faceted tips, which indicates that an individual column has a single crystal structure. This observation
was confirmed by our recent work [20] and previous studies [21-23] which reported that individual metallic nanorods fabricated by GLAD are typically single crystal. Single-crystal rods do not have interior grain boundaries and have faceted sharp tips [24]. This property will allow enhanced electrochemical activity and reduced surface oxidation [25], which can greatly increase the robustness and resistance to oxidation-degradation of the electrode layer in the fuel cell environment.

Figure 1: Top and cross-section scanning electron microscopy (SEM) views of 200 nm long GLAD Pt nanorod arrays.

The QCM setup was used to measure the Pt loading of the prepared samples. We measured the weight loading of 200 nm long Pt nanorods to be about 0.16 mg/cm$^2$. Based on these QCM measurements, we calculate that the weight loading of Pt nanorods can be set to as low as 0.8 $\mu$g/cm$^2$ per nanometer length of the rods.

Figure 2: X-ray diffraction (XRD) profiles of 200 nm long GLAD Pt nanorod arrays.

The XRD results in Fig. 2 reveal that the Pt nanorods are mainly oriented in the [200] direction, which is equivalent to the [100] direction perpendicular to the substrate. The (100) texture of Pt nanorods obtained from $\theta$-2$\theta$ XRD scans indicate the dominant Pt(100) crystal planes in the bulk of the rods parallel to the substrate and cannot provide any direct information on the crystal planes on the nanorod surface (tip-facets and sidewalls). In our previous work [26], we showed that GLAD Pt nanorods are highly hydrophilic enabling penetration of aqueous electrolyte and/or ionomer into the nanorod arrays and interaction of the electrolyte with the high-surface-area side walls of the nanorods. Therefore, we have recently performed pole-figure
measurement which showed that the sidewalls of the nanorods, which dominate the overall surface area of the nanorods, are mainly in the [110] orientation. Moreover, it has been found that the facets of the nanorod tips have [111], [100], and [110] orientations [20]. The nanorods are expected to have a large fraction of (110) planes because these are the dominant planes at the high-surface-area nanorod sidewalls. Hence, we believe that the dominant exposed plane of the nanorods is Pt(110), the plane that is the most active for the ORR [10,11].

![Figure 3: Room temperature CV plots of (a) conventional (Pt/C) in 0.1 O2-free M HClO4 at a scan rate of 50 mV/s; first cycle and after 1000 cycles and (b) 200 nm long Pt nanorods in 0.1 O2-free M HClO4 at a scan rate of 50 mV/s over first cycle and 2000 cycles.](image)

Room temperature CV plots of 200 nm long Pt nanorods as well as Pt/C electrocatalysts are shown in Fig. 3. All the prepared samples were scanned between 0 and 1.15 V in 0.1 M HClO4 at a scan rate 50 mV/s. Compared to Pt/C, Pt nanorods exhibit a more positive oxide reduction peak potential, indicating that the GLAD Pt nanorods are less oxophilic. The 200 nm Pt nanorods and conventional Pt/C samples were also scanned multiple times in the 0.6 to +1.0 V range at a scan rate 50 mV/s to establish their stability in the acidic environment. A series of CVs from 200 nm Pt nanorods over 2000 cycles and a series of CVs from Pt/C over 1000 cycles at room temperature were obtained. It was found that the CV current of Pt/C decreases considerably (40% area loss) as shown in Fig. 3(a), which reflects the loss of Pt surface area, while the 200 nm Pt nanorods shows insignificant change (22% area loss) in the CV current, indicating the superior stability of the nanorod catalyst over fuel cell relevant potentials.

CV was also employed to calculate the electrochemical active surface area (ECSA) of Pt/C and Pt nanorods catalysts. ESCA was determined at room temperature (20 °C) from the
integration of the hydrogen adsorption and desorption regions. Assuming 210 \( \mu \text{C/cm}^2 \) Pt surface area for a full monolayer of adsorbed hydrogen (saturation coverage) and after double-layer and hydrogen evolution corrections, ECSA were calculated from the following equation [27]:

\[
\text{ECSA}(\text{cm}^2 \text{Pt} / \text{gPt}) = \frac{C_{\text{Hg}} e(\mu \text{C/cm}^2)}{210(\mu \text{C/cm}^2) \text{Pt}_{\text{loading}} (\text{gPt/cm}^2)}
\]  \tag{1}

The results show that the ECSA of 200 nm long Pt nanorods with Pt loading of 0.16 mg/cm\(^2\) is 12 m\(^2\) Pt/g Pt. Conventional Pt/C electrode exhibits ECSA of 65 m\(^2\)Pt/g Pt at a Pt loading of 0.02 mg/cm\(^2\), which is higher than that of the Pt nanorod electrocatalyst. The ECSA value of Pt/C electrocatalyst is in good agreement with the reported values in the literature [7].

In order to obtain an accurate comparison for high surface area catalysts, detailed room temperature RDE measurements in oxygen-saturated 0.1 M HClO\(_4\) at a scan rate 20 mV/s and rotation rate 1600 rpm were performed on Pt/C and Pt nanorods (Fig. 4) for calculating the most important kinetics parameters: Pt mass-specific activity and area-specific activity which are the accepted measures of true catalytic activity towards ORR [7]. The kinetic current can be determined using the well-known mass-transport correction for RDE measurements [7,29):

\[
I_k = \left( \frac{I_{\text{lim}} \times I}{I_{\text{lim}} - I} \right)
\]  \tag{2}

where \( I \) is the measured current at a specified potential, \( I_{\text{lim}} \) is the measured limiting current, and \( I_k \) is the kinetic current. Specific activities can be determined by calculation of \( I_k \) using Eq. (2) and normalization to measured Pt ECSA and Pt loading. The area and mass specific activities for Pt/C and Pt nanorods were calculated at 0.9 V (vs. RHE) and are reported in Table 1. In addition, the reported values of area and mass specific activities taken from the literature [29] are shown for comparison. The area and mass specific activities measured for Pt/C are in good agreement with the values reported in the literature [7,29]. The area-specific activity of the Pt nanorod electrocatalyst was found to be higher than that of Pt/C and NSTF Pt and comparable to that of polycrystalline Pt. As explained in the introduction, ORR activity in 0.1 M HClO\(_4\) electrolyte follows the trend Pt(110)\(>\)Pt(111)\(>\)polycrystalline Pt\(>\)Pt(100) [10,11]. Because the side walls of the Pt nanorods are dominated by (110) planes, one would expect a higher area-specific ORR activity for GLAD nanorods compared to polycrystalline Pt. Polycrystalline Pt-like ORR activities may be due to the existence of Pt(100) planes at the sidewalls and tips of some of the nanorods and to the presence of low coordination sites at the edges of the low index planes, which can reduce the electrochemical activity compared to that of ideal pure Pt(110) in perchloric electrolyte. It should be noted that the existence of Pt(100) planes is expected to improve ORR electrocatalytic activity in adsorbing electrolytes such as sulfuric acid or perfluorosulfonic acid fuel cell electrolyte (e.g., Nafion) [30,31], as explained in the introduction section. Therefore, in addition to the effects of electrochemically active Pt(110) planes of Pt nanorods discussed above, the higher area-specific activity of the 200 nm GLAD Pt nanorods can be attributed in part to their larger crystallite dimensions compared to Pt/C and to NSTF Pt. However, the large crystallite size of the Pt nanorod as well as NSTF Pt catalysts compared to Pt/C results in a lower ratio of surface to bulk Pt atoms and consequently lower mass activity than Pt/C, as shown Table 1.
Finally, the slight decrease in the limiting current of Pt/C at potentials less than 0.20 V (Fig. 4), in the region of hydrogen adsorption, indicates the formation of H$_2$O$_2$ and a change in the ORR pathway from a four- to a two-electron mechanism [10]. This change in the mechanism is less pronounced in the case of Pt nanorods (i.e. hydrogen peroxide production rate on Pt nanorods is lower than that of Pt/C) as can be seen in Fig. 4, indicating that the contribution from the two-electron process at <0.2 V is lower for the nanorods. This observation is similar to what was seen for single-crystal Pt(110) electrodes [10].

Table 1: Summary of the evaluated electrocatalytic activity (area-specific and mass-specific activities at 0.9 V vs. RHE) of Pt nanorod arrays catalyst in 0.1 M HClO$_4$ and comparison to the literature values for various Pt catalysts.

<table>
<thead>
<tr>
<th>Method</th>
<th>Sample Description</th>
<th>Pt loading (mg/cm$^2$)</th>
<th>ECSA (m$^2$/g)</th>
<th>T ($^\circ$C)</th>
<th>Scan rate (mV/s)</th>
<th>$I_u$ (μA/cm$^2$)</th>
<th>$I_m$ (A/mg)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>RDE</td>
<td>200 nm long Pt nanorods</td>
<td>0.16</td>
<td>12</td>
<td>20</td>
<td>20</td>
<td>1060</td>
<td>0.127</td>
<td>This work</td>
</tr>
<tr>
<td>TF-RDE</td>
<td>20% Pt/C, d=3-5 nm</td>
<td>0.02</td>
<td>65</td>
<td>20</td>
<td>20</td>
<td>260</td>
<td>0.17</td>
<td>This work</td>
</tr>
<tr>
<td>TF-RDE</td>
<td>Bulk Poly-Pt</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>20</td>
<td>1200</td>
<td>-</td>
<td>[29]</td>
</tr>
<tr>
<td>TF-RDE</td>
<td>NSTF Pt</td>
<td>0.042</td>
<td>8</td>
<td>20</td>
<td>20</td>
<td>750</td>
<td>0.06</td>
<td>[29]</td>
</tr>
</tbody>
</table>
CONCLUSION

Vertically aligned platinum nanorod arrays produced by the GLAD technique were investigated for their ORR electrocatalytic activity. It was found that Pt nanorod electrocatalyst exhibits higher area-specific activity and greater stability against electrochemically-active surface area loss than conventional Pt/C. The enhanced ORR activity of Pt nanorods is attributed to their larger crystallite size, single-crystal property, and the dominance of (110) crystal planes on the nanorod sidewalls, which has been found to be the most active plane for ORR. However, the mass-specific ORR activity of the Pt nanorods was found to be lower than that of the Pt/C catalyst, mainly due to the large diameter of nanorods. Using alternative engineering approaches such decreasing the diameter of the nanorods, thereby increasing the surface/bulk atom ratio, and chemical approaches, such as alloying, the Pt mass-specific activity can potentially be improved. These approaches may open the way for utilizing GLAD nanorods as cathode material in PEM fuel cells.

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REFERENCES